

# Formation of the $S = 1$ paramagnetic centers in the bond-diluted spin-gap magnet.

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**Abstract.** Electron spin resonance experiment reveals that non-magnetic bond doping of the spin-gap magnet  $(\text{C}_4\text{H}_{12}\text{N}_2)\text{Cu}_2\text{Cl}_6$  (abbreviated PHCC) results in the formation of  $S = 1$  paramagnetic centers that dominate low-temperature ESR response. We have followed evolution of this signal with doping impurity content and have found that these centers concentration is quadratic over the impurity content. We also observe coexistence of the ESR responses from these local centers and from delocalized triplet excitations over certain temperature range.

PACS numbers: 75.10.Kt, 76.30.-v

Submitted to: *JPCM*

## 1. Introduction

Spin-gap magnets have been actively studied during the last decades. These systems are characterized by the presence of a nonmagnetic singlet ( $S = 0$ ) ground state separated from the excited triplet ( $S = 1$ ) states by an energy gap  $\Delta$  of exchange origin. One of the most striking features of these systems is that despite strong exchange coupling they do not order magnetically down to lowest temperatures.

Stability of the singlet ground state against various perturbations: additional spin-spin interactions, external magnetic field, pressure and introduction of impurities is a long discussed problem. Magnetic field lifts degeneracy of the triplet states and splits triplet sublevels. At the critical field  $H_c = \Delta/(g\mu_B)$  energy of one of the triplet sublevels becomes lower than the energy of the singlet ground state. At this point phase transition occurs which was actively discussed in the context of Bose-Einstein condensation of magnons [1, 2].

Impurities can substitute magnetic ions depleting magnetic system (site-doping) or alternate superexchange pathes (bond-doping). Impurity ions vary material properties locally disturbing and sometimes even destroying the spin-gap state of the parent material. This leads to the variety of known effects. Formation of the impurity induced magnetic order was observed in a spin-Peierls magnet  $\text{CuGeO}_3$  [3, 4], Haldane magnet [5] or a prototypical dimer magnet  $\text{TiCuCl}_3$  [6, 7]. Randomization of the exchange couplings through the bond doping allows for possibility of realization of a Bose-glass state [8, 9] or a universal low-energy physics of a random spin chain [10, 11, 12].

Violation of the gapped state in the impurity vicinity can lead to a formation of a multi-spin defects with total non-zero spin. These defects (or spin clusters) can demonstrate unusual properties: Spin clusters in Ni-doped spin-Peierls magnet  $\text{CuGeO}_3$  demonstrated unusual (as small as 1.4) and highly-anisotropic  $g$ -factor [13, 14, 15]. Spin clusters formed at the ends of the chain fragment of a Haldane  $S = 1$  magnet are shown both theoretically [16] and experimentally [17, 18, 19] to carry total spin  $S = 1/2$  each.

Our recent study [20] demonstrated that bond-doping in the quasi-2D spin-gap magnet  $(\text{C}_4\text{H}_{12}\text{N}_2)\text{Cu}_2\text{Cl}_6$  (abbreviated PHCC) leads to the formation of yet another type of defect: a local  $S = 1$  defect. This is a surprising outcome, as magnetic ions of PHCC are antiferromagnetically coupled  $S = 1/2$   $\text{Cu}^{2+}$  ions. Effect of bond-doping in this case can be interpreted as variation of the effective potential acting on the triplet quasiparticles (which are freely moving quasiparticles in a pure system). As there is always a bound state in a 2D potential well, one can expect that some of triplet excitations could be trapped in the defect vicinity if this effective potential is attractive. In the case of bromine-substituted PHCC this potential turns out to be not only attractive, but strong enough to yield a low-lying bound state. In the present report we demonstrate new experimental findings that provides additional proof of this effect.

## 2. Samples and experimental details

Samples of Br-substituted PHCC  $(\text{C}_4\text{H}_{12}\text{N}_2)(\text{Cu}_2\text{Cl}_{6(1-y)}\text{Br}_{6y})$  were grown from the solution as described in Ref. [21]. We used samples from the same set as were used in Refs. [24, 25, 20, 26, 27]. We will use nominal Br concentration  $x$  for sample identification as it was used in earlier papers.

PHCC crystallizes in a triclinic structure, as-grown crystals are elongated along the  $c$ -axis and has a well developed plane orthogonal to  $a^*$  direction. As PHCC became almost non-magnetic at low temperatures large crystals (approx.  $2 \times 3 \times 6\text{mm}^3$ ) were used which limited mounting possibilities in our experimental setup. To compare data with earlier work, we mounted samples in the  $\mathbf{H}||a^*$  orientation (field applied orthogonal to the natural plane of the crystal).

Magnetic ions  $\text{Cu}^{2+}$  form planes in the  $(ac)$  crystallographic plane of PHCC. Inelastic neutron scattering studies [22, 23] indicates presence of 6 to 8 relevant in-plane exchange bonds. Geometry of the exchange bonds can be envisioned as a set

of strongly coupled ladders with dominating in-rung exchange and some frustrating couplings. Thus, a dimer  $\text{Cu}_2\text{Cl}_6$  with the strongest antiferromagnetic exchange coupling (bond 1 in terms of Ref. [23]) can be considered as a building block of the PHCC magnetic structure. Intra-dimer exchange is mediated by two halogen ions.

Up to nominal bromine concentration of 12% crystals remain single-phase. Detailed structural analysis of Ref. [24] have demonstrated that occupancy of different halogen sites differs from the nominal concentration. However, actual occupancy of all sites is linear with nominal concentration of the bromine. Average actual bromine concentration is [24]  $y = 0.63x$ .

ESR absorption was studied using set of homemade transmission type spectrometers in the temperature range from 400mK to 20K. Microwave power transmitted through the microwave cavity with the sample depends upon imaginary part of susceptibility as  $P_{trans}(H) \propto 1/(1 + A\chi''(H))^2$ , here factor  $A$  depends upon experimental conditions (cavity Q-factor and sample position inside the cavity) and is the same within given experiment. ESR absorption can be scaled with static magnetization data since paramagnetic resonance integral intensity  $I = \int \chi''(H)dH$  is proportional to the static susceptibility.

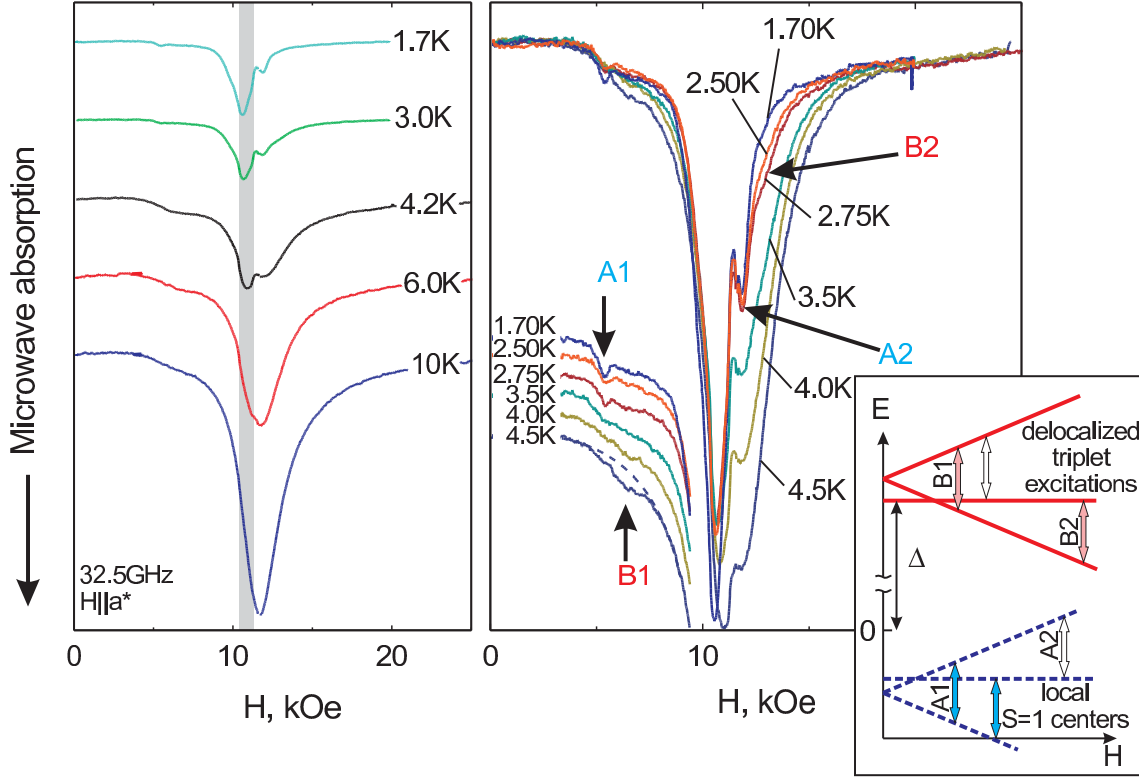
ESR is a sensitive tool to probe low-energy dynamics of a magnet. In the case of a  $S = 1$  magnetic ion or a triplet excitation of the spin gap magnet anisotropic interactions lead to the zero-field splitting of the triplet level. This splitting is described by the term  $DS_z^2$  in the spin Hamiltonian in the axial case and by a terms  $DS_z^2 + E(S_x^2 - S_y^2)$  in a general case. In the case of weak splitting magnetic field direction is a quantization axis and effective anisotropy constants  $D$  and  $E$  are orientation dependent. We will assume axial anisotropy (i.e.,  $E = 0$ ) in the qualitative discussions of this paper.

As a result of zero-field splitting resonance fields in the fixed-frequency experiment differ for  $|S_z = +1\rangle \rightarrow |S_z = 0\rangle$  and  $|S_z = -1\rangle \rightarrow |S_z = 0\rangle$  transitions as  $H_{1,2} = H_0 \pm D/(g\mu_B)$ , here  $H_0 = \hbar\omega/(g\mu_B)$  is a paramagnetic resonance field for the given  $g$ -factor. At low temperatures intensities of these components are different, component corresponding to the transition from low-energy sublevel dominates. At  $\mathbf{H}||z$ , left component ( $H = H_0 - |D|/(g\mu_B)$ ) is more intense at  $D < 0$ , while right component dominates at  $D > 0$ . Additionally, a characteristic "two-quantum" absorption corresponding to  $|S_z = +1\rangle \rightarrow |S_z = -1\rangle$  transition appears in the field  $H_{2q} = H_0/2$ . This transition is forbidden in the axial case but it becomes allowed if magnetic field deviates from the anisotropy axis or if  $E \neq 0$ . The "two-quantum" absorption is a fingerprint of an  $S = 1$  magnetic center.

### 3. Experimental results and discussion

#### 3.1. Summary of the earlier results.

Energy spectrum of the doped PHCC was studied on the samples from the same set as the samples earlier studied by means of inelastic neutron scattering [26, 27]. INS

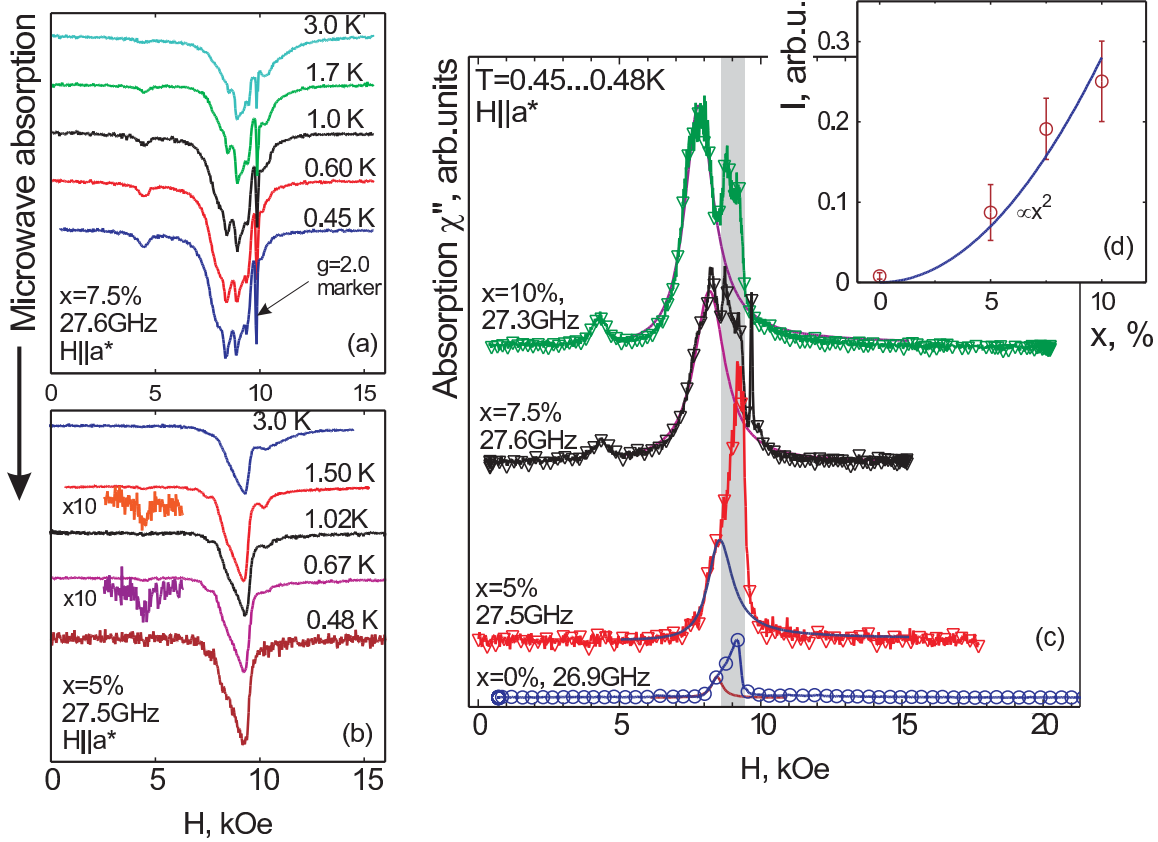


**Figure 1.** Temperature dependence of the ESR absorption in a Br-substituted PHCC with nominal Br concentration  $x = 7.5\%$ . Left panel: representative data in the broad temperature range. Shaded area marks position of absorption due to uncontrolled defects as estimated from 3.0K data. Right panel: selection of low-temperature (below 4.5K) ESR absorption curves illustrating development of ESR response from local  $S = 1$  centers. Components of the ESR absorption related to local  $S = 1$  centers are denoted as "A1" and "A2", components of the ESR absorption corresponding to gapped triplet excitations are denoted as "B1" and "B2". Inset to the right panel: scheme of the zero-field splitting of triplet state for the triplet excitations (solid lines) and for the local  $S = 1$  centers (dashed), position of the singlet state is not shown, magnetic field is assumed parallel to the anisotropy axis for both sorts of triplets. Broad vertical arrows marks possible ESR transitions, filled arrows corresponds to the transitions from the lowest sublevel. ESR transitions are marked as the corresponding absorption components.

study demonstrates that excitation spectrum of the bromine substituted PHCC remains gapped, energy gap increases with doping being equal to 1 meV for the pure PHCC and 1.5 meV for  $x = 7.5\%$  [26].

ESR absorption in pure and bond-diluted PHCC was reported in Refs. [25, 20]. Magnetic resonance response of a spin-gap magnet is a combination of a signal from triplet excitations and paramagnetic defects. These two contributions can be resolved due to their characteristic temperature dependences.

At temperatures above 10K magnetic resonance absorption spectra in pure and doped PHCC is dominated by a Lorentzian line with anisotropic  $g$ -factor slightly above



**Figure 2.** Low-temperature ESR absorption in Br-substituted PHCC. (a),(b) Representative ESR absorption spectra for the samples with nominal Br concentration  $x = 5, 7.5\%$ . (c) Comparison of the scaled microwave absorption at the base temperature of the cryostat ( $T = 0.45 \dots 0.48$  K) for different bromine concentration. Lines with symbols are experimental curves, solid lines are Lorentzian fits. Scaling procedure is described in the text. Data are offset for better presentation. Shaded area marks ESR absorption by the uncontrolled defects which was excluded from the fit procedure. (d) Concentration dependence of the intensity of the impurity-induced absorption.

2.0, as is typical for a  $\text{Cu}^{2+}$  ion. On cooling below 10 K intensity of the ESR absorption decreases as triplet excitations freeze out. At low temperatures (below approximately 4 K) gas of triplet excitations is diluted, effects of quasiparticles interaction are switched off and ESR absorption spectrum transforms into a multi-component absorption typical for the  $S = 1$  object in the presence of anisotropy. This spectrum consists of two intense components shifted to the left and to the right from the higher temperature resonance position and of one weaker component at approximately half of the higher temperatures resonance field ("two-quantum" absorption). For the pure PHCC these split components continue to lose intensity on cooling and ESR absorption at lowest temperatures consists of paramagnetic impurities (termed uncontrolled defects for the remainder of the paper) response only [25].

In the case of strongly doped PHCC with nominal bromine concentration  $x = 10\%$

low temperature evolution of ESR absorption was quite distinct. ESR absorption typical for a  $S = 1$  object was observed down to 500 mK. Temperature dependence of the intensity of this low-temperature absorption was described assuming presence of approximately 0.4% of gapless  $S = 1$  centers (gapless triplets) per molecule of PHCC [20]. These gapless triplets were interpreted as localized triplet modes caught in the potential well created by double substitution of a chlorine ions by bromine in a dimer.

While ESR absorption spectra of  $x = 5\%$  Br-substituted sample above 1.7K have demonstrated similar tendency [20], there were no low-temperature (below 1 K) data to prove it unambiguously. Also data for an intermediate bromine concentration were missing. In the following sections we will close these lacunas.

### *3.2. Coexistence of ESR absorption from local $S = 1$ centers and delocalized triplets.*

Firstly, we will demonstrate here that ESR absorption spectra of the intermediately bromine-substituted sample with  $x = 7.5\%$  provides evidences for coexistence of the triplet absorption from the gapped delocalized triplets and local  $S = 1$  centers over a certain temperature range. Such coexistence indicates that gapped triplets and local  $S = 1$  centers are actually different objects decoupled at low temperatures.

Evolution of the ESR absorption in the 7.5% nominally substituted sample is presented in Figure 1. At 10K main absorption signal is almost a single-component paramagnetic resonance with remnants of the "two-quantum" absorption visible. On cooling ESR absorption shape became distorted. At 4.2K "two-quantum" absorption becomes more pronounced, irregularly shaped paramagnetic absorption appears and main absorption signal broadens and splits. Boundaries of paramagnetic resonance absorption due to uncontrolled defects can be estimated from low temperature data, this signal has quite distinguishable powder-like shape (see also data for nominally pure sample in Figure 2 for comparison). These boundaries are shaded in Figure 1. On further cooling components of the main absorption signal continue to loose intensity and around 2K they are replaced by another more narrow signal. The same evolution can be traced for the "two-quantum" transition.

At the intermediate temperatures coexistence of these two sorts of signals can be followed (see right panel of Figure 1): with cooling narrow components (labeled as "A1" and "A2") gain intensity and broad components (labeled as "B1" and "B2") lose intensity. Both sorts of signals correspond to the  $S = 1$  objects, "two-quantum" transition being the main fingerprint. Signals "B1" and "B2" disappearing with cooling are naturally related to the gapped delocalized triplet excitations. Signal that gains intensity with cooling is due to the local  $S = 1$  centers.

At the lowest temperature of 1.7K spectral weight is shifted to the left from the paramagnetic resonance position. This is in agreement with earlier observations on pure and 10% nominally doped PHCC: for the pure compound (delocalized triplets only) right component of the split signal is more intense, while low-temperature absorption in the 10% doped sample (which was due to the local  $S = 1$  centers) was dominated by its left

component.

This difference in the position of more intense component correspond to different sign of effective anisotropy constant for the delocalized triplets and local  $S = 1$  centers. Note, that there is no single-ion anisotropy effects for the  $S = 1/2$  copper ions of PHCC — thus, these effective anisotropy constants both for the delocalized excitations and for the local  $S = 1$  centers are due to some anisotropic spin-spin interactions.

### *3.3. Concentration dependence of the low-temperature absorption*

Here we will compare low-temperature absorption from different samples below 1K, when all absorption is due to the uncontrolled defects and local  $S = 1$  centers.

Low-temperature ESR absorption spectra are shown in Figure 2. We observe several absorption components: characteristic powder-like absorption due to uncontrolled defects, split absorption due to the  $S = 1$  centers and weaker "two-quantum" absorption signal at approximately half of the paramagnetic resonance field. Uncontrolled paramagnetic impurities yield irregularly shaped absorption signal at almost the same fields, which complicates extraction of the localized triplets response. However, boundaries of this absorption are approximately the same (at the same microwave frequency) and can be reliably established from the analysis of all data (see shaded area in Figure 2-c).

To compare absorption curves measured on different samples we have extracted imaginary part of the susceptibility and scaled its integral at temperature of 3-5K to the known static susceptibility data. This procedure allowed to recalculate absorption for different samples to the same scale. Scaled curves demonstrate regular increase of absorption to the left of the paramagnetic resonance field with increase of bromine concentration. This absorption corresponds to one of the split components of local  $S = 1$  centers.

To analyze intensity of the split components we have to separate contribution from uncontrolled defects, which is clearly complicated at low bromine content. Weaker "two-quantum" signal is well separated from the paramagnetic impurities signal, however it is impossible to compare its intensity in different samples as intensity of this "almost forbidden" transition strongly depends on excitations conditions which were not reproducible. Absorption in the vicinity of paramagnetic resonance on the contrary is excited by usual transverse polarization which allows to scale it with static magnetization data. To exclude uncontrolled impurities signal we simply ignored data in its vicinity (shaded area in Figures 1 and 2) during the fit.

As a result of the fit intensities of the ESR absorption due to the localized triplets were found. Accuracy of intensity determination is about 20% being hindered by uncertainties of the scaling procedure and some arbitrariness in the paramagnetic signal exclusion. To check the reliability of this procedure we made similar fit for the nominally pure sample, which yielded possible contribution tenfold smaller than for the  $x = 5\%$  sample.

Intensity of the split component is proportional to the concentration of  $S = 1$  objects. It approximately follows  $x^2$  dependence thus supporting the model of double substitution in a dimer suggested in Ref. [20].

Position of the split component to the left from paramagnetic resonance position again corresponds to the inversion of effective anisotropy constant sign for the local  $S = 1$  centers as compared to triplet excitations (see energy levels scheme at Figure 1). Magnitude of the shift from the paramagnetic resonance position is slightly concentration dependent: splitting increases with increasing bromine content. Variation of this splitting with bromine content is not unexpected: doping slightly modifies lattice parameters [24] which could lead to modification of anisotropic spin-spin couplings.

#### 4. Conclusions

We have demonstrated that  $S = 1$  centers are formed in a spin-gap magnet PHCC with non-magnetic bond-doping. These centers are presumably formed from a couple of  $S = 1/2$   $\text{Cu}^{2+}$  ions on double substitution of intra-dimer chlorine by bromine. We have shown that at low temperatures these centers are decoupled from the triplet excitations and that the effective anisotropy constant for local  $S = 1$  centers differs from that for the triplet excitations.

The work was supported by Russian Foundation for Basic Research Grant No.15-02-05918. This work was partially supported by the Swiss National Science Foundation, Division 2 and by the Estonian Ministry of Education and Research under grant No. IUT23-03 and the Estonian Research Council grant No. PUT451.

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